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Tetraalkylammonium *N*-chloro-*p*-toluenesulfonamide as aminating agent of olefins

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Abstract

The alkylammonium salt of chloramine-T has been used as aminating agent of olefins in the presence of M(TPP)Cl (M = Fe, Mn; TPP = tetraphenylporphyrin) as catalyst. Main products were the corresponding allylamine, the aziridine, the α-chloro-amine derived by attack of chloride ion on the less substituted carbon of the aziridine, and toluene-*p*-sulfonamide. The reaction gave reasonable yields of the products with unsubstituted cyclic olefins, while poor results have been obtained with norbornene and 1-hexene. © 1997 Elsevier Science B.V.

Keywords: Tetraalkylammonium N-chloro-*p*-toluenesulfonamide; Metalloporphyrins; Amination; Olefins

1. Introduction

Recently tosylimidoiodobenzene derivatives, ArI = NTs [1], the tosylimide analogue of iodosobenzene, have been employed for the amination of saturated and unsaturated hydrocarbons, by using manganese(III) and iron(III)-porphyrins as catalysts [2–5]. The best results have been obtained with alkenes as substrates, obtaining the corresponding aziridines [3,4] and/or allylamines [5] in good yields. Main by-product of these reactions is the corresponding sulfonamide, $TsNH_2$, which is presumably derived by hydrolysis of a possible metal–nitrene intermediate. This point emphasizes the importance of using dry conditions in these reactions.

The azidirination reaction resulted stereospecific by using $Fe(TDCPP)ClO_4$ as catalyst (TDCPP = tetrakis-2,6-dichlorophenylporphyrin) [4]. Reaction of PhI = NTs with Fe(TPP)Cl (TPP = tetraphenylporphyrin), allowed the isolation of an iron(III) porphyrin complex with the nitrene moiety inserted into a Fe–N bond, Fe(TPP)(NTs)Cl [6,7]. Tosylimidoiobenzene derivatives are prepared by reaction of diacetoxyiodoarenes, $ArI(OAc)_2$, with the corresponding amides under basic conditions [1,8,9]. Diacetoxyiodoarenes are obtained by oxidation of iodobenzene with peracetic acid. On the other hand, the related iminoderivative, chloramine-T, $[Na][4\text{-}MeC_6H_4SO_2NCl] \cdot 3H_2O$, can be read-

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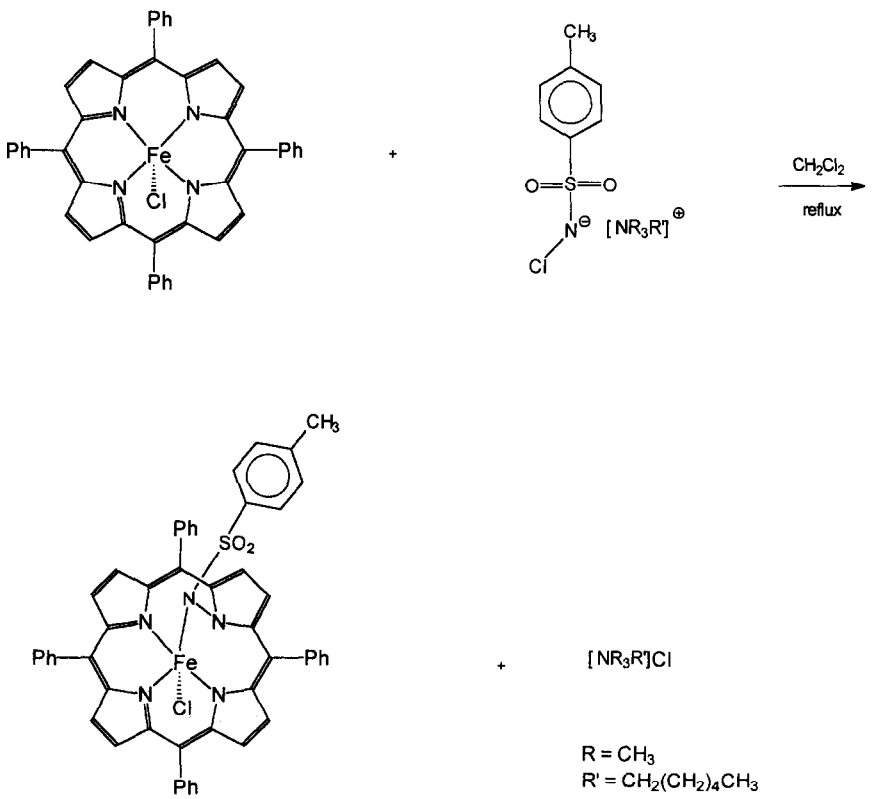
ily obtained by reaction of the arylsulfonamide with sodium hypochlorite [10]. Chloramine-T has been used as aminating agent of hydrocarbons in the presence of ferrous chloride in stoichiometric reactions [11]. Catalytic, vicinal oxyamination of olefins by chloramine-T has been achieved by using OsO_4 as catalyst [12,13]. Phase transfer catalysis is ideal for the oxyamination of monosubstituted and sym-disubstituted olefins [13]. α-aminoaldehydes have been obtained from enamines and chloramine-T [14]. The catalytic, asymmetric aminohydroxylation of olefins has been obtained by using chloramine-T as aminating agent, $K_2OsO_2(OH)_4$ as catalyst and chiral ligands [15]. Allylic amination of olefins has been carried out with anhydrous chloramine-T and selenium metal [16]. Drawback of the use of chloramine-T as aminating agent is its poor solubility in the common organic solvents and the presence of three molecules of water per molecule of compound. The presence of water is not an inconvenient when hydroxyamination reactions are carried out, but it is undesirable when products of the reaction are compounds such as allylamines and aziridines. Anhydrous chloramine-T can be obtained by careful thermal dehydration in vacuo of the hydrate [10,11,16]. However this procedure is dangerous since anhydrous chloramine-T is explosive, and, moreover, does not solve the problem of the low solubility of this compound in common organic solvents. We considered that both these problems can be avoided by using an alkylammonium salt of *N*-chloro-*p*-toluene sulfonamide [17]. We report here on the use of this aminating agent with several olefins



Scheme 1.

and transition metal compounds such as manganese(III) and iron(III)-porphyrins, as activating metal centers.

2. Results and discussion

2.1. Ammonium salt of chloramine-T as nitrene source

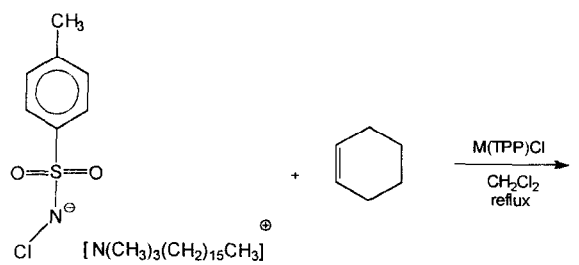
We verified that the ammonium salt of chloramine-T can act as a nitrene source, by its reaction with Fe(TPP)Cl [6,7] (Scheme 1):

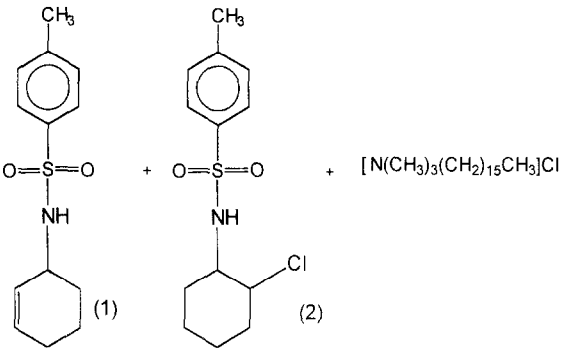
From this reaction, the bright purple iron(III) complex with the nitrene moiety inserted into a Fe–N bond, Fe(TPP)(NTs)Cl, has been isolated. This compound showed an elemental analysis and ^{1}H NMR spectrum in accordance with what reported by Mansuy, for the product of the reaction of Fe(TPP)Cl with TsN = IPh [6,7].

It is worth mentioning here that while the ammonium salt of chloramine-T is reported in Scheme 1 as having the negative charge localized on nitrogen, it probably has the negative charge mainly localized on the oxygen atoms of the sulfonyl group, as it has been demonstrated by the X-ray structural determination of chloramine-T trihydrate [18].

2.2. Catalytic reactions

By reaction of the ammonium salt of chloramine-T with cyclohexene in refluxing methylene chloride and with M(TPP)Cl(M = Fe, Mn) as catalyst, we isolated the corresponding allylamine (**1**) and α-chloroamine (**2**) (Eq. (1)) (Table 1):





(1)

Substantial amounts of $TsNH_2$ (ca. 40–50% of the starting ammonium salt) are also formed, even if the reaction has been conducted in dry solvent, in the presence of molecular sieves and under a dinitrogen atmosphere in order to avoid the presence of moisture. The α-chloroamine (**2**) is probably derived by attack of the chloride ion of the alkylammonium salt present in the solution to an intermediate aziridine. It is known that this reaction is favoured by electron withdrawing groups present as substituents at the nitrogen atom of the aziridine [19]. The α-chloroamine is also present when the reaction is carried out in CH_3CN, thus excluding that methylene chloride is responsible for the chlorination reaction. The aziridine derivative has been observed when cyclooctene has been used as substrate (Table 1). With cyclopentene as substrate again the aziridine was absent (Table 1).

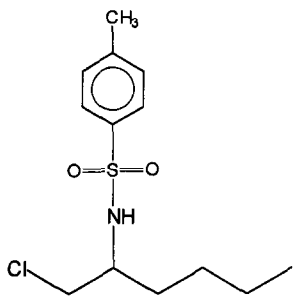
Table 1

Olefin	Product	Yield (%) [a,b]	
		Fe(TPP)Cl	Mn(TPP)Cl
Cyclohexene	allylamine (**1**) [11]	18.7	22.1
	α-chloroamine (**2**) [11]	13.5	16.8
cyclooctene	allylamine (**3**) [5]	7.2	9.2
	aziridine (**4**) [5]	8.5	10.3
	α-chloroamine (**5**)	5.4	8.1
cyclopentene	allylamine (**6**)	15.4	19.1
	α-chloroamine (**7**) [21]	5.2	6.1

[a] Calculated with respect to the starting ammonium salt of chloramine-T.

[b] Reaction carried out for one hour, at reflux in dry CH_2Cl_2 (2 ml), with the olefin (5.5–7.5 ml), the aminating agent and the catalyst in a 2000:20:1 ratio.

With an olefin such as norbornene, small amounts of the corresponding aziridine (1.5–2.5%) and traces of the α-chloroamine have been isolated. In this case the allylamine was absent, in accordance with the slow formation of a bridgehead allylic radical [20]. Finally, with a linear olefin such as 1-hexene, only the α-chloroamine (**8**) (6.5–9%) was obtained, with traces of the allylamine. The α-chloroamine has probably the structure:



in accordance with the fact that the chloride ion preferentially attacks the less substituted carbon of the intermediate aziridine. The proposed structure is confirmed by the ^{1}H NMR data.

3. Conclusions

In this preliminary work we have shown that the alkylammonium salt of chloramine-T can be used as aminating agent of unsubstituted cyclic olefins, in a reaction catalyzed by manganese(III) and iron(III)-porphyrin derivatives. With a linear olefin such as 1-hexene, the reaction did not give good results. Yields of the products were comparable to those obtained by using tosylimidoiodobenzene derivatives as aminating agent [3–5], on considering that the intermediate aziridine is in part converted into the corresponding α-chloroamine. On the other hand, the dry alkylammonium salt of chloramine-T is easy to prepare and can be handled without any particular care.

4. Experimental

Elemental analyses have been carried out on a Perkin Elmer 2400 CHN Elemental Analyser. ^{1}H NMR spectra were obtained using a Brucker AC-200 (200 MHz) spectrometer. Solvents and reagents were distilled prior to use. The iron–porphyrin–nitrene complex was synthesized using the tetraalkylammonium salt of *N*-chloro-*p*-toluenesulfonamide according to a described procedure [7]. The tetraalkylammonium salt of *N*-chloro-*p*-toluenesulfonamide was prepared as reported in Ref. [17].

After evaporation of the solvent, all crude reaction products were purified by flash chromatography using CH_2Cl_2/hexane 9/1 as eluant.

4.1. Compound (5)

^{1}H NMR ($CDCl_3$, ppm): 7.81(2H, d, $J = 8.3$ Hz), 7.31(2H, d, $J = 8.3$ Hz), 4.92 (1H, s, broad), 4.3 (1H, m), 3.93 (1H, m), 2.31(3H, s), 2.21–1.53 (12H, m); MS(*m/z*, EI, 70 eV): 317, 315, 280, 210, 197, 184,173, 155, 124, 91, 76.

4.2. Compound (6)

^{1}H NMR ($CDCl_3$, ppm): 7.83(2H, d, $J = 9.1$ Hz), 7.36(2H, d, $J = 9.1$ Hz), 5.71 (1H, d, $J = 10.5$ Hz), 5.31 (1H, m), 4.34(1H, s, broad), 3.73 (1H, m), 2.34(3H, s), 2.11–1.51 (4H, m); MS(*m/z*, EI, 70 eV): 237, 196, 173, 155, 91, 76.

4.3. Compound (8)

^{1}H NMR ($CDCl_3$, ppm): 7.79(2H, d, $J = 8.5$ Hz), 7.34(2H, d, $J = 8.5$ Hz), 4.86 (1H, s, broad), 4.28 (1H, m), 2.31(3H, s), 1.98–1.11 (11H, m); MS(*m/z*, EI, 70 eV): 291, 289, 253, 91, 76.

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